Jurnal Teknologi Industri Pertanian
25 (3):239-247 (2015)

TRANSESTERIFICATION OF CALOPHYLLUM OIL (*Calophyllum inophyllum* L) BY CALCIUM OXIDE CATALYST : OPTIMIZATION AND KINETIC MODEL

TRANSESTERIFIKASI MINYAK NYAMPLUNG (Calophyllum inophyllum L) DENGAN KATALIS KALSIUM OKSIDA : MODEL OPTIMASI DAN KINETIKA

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Paper: Received 27 October 2014; Revised 26 March 2015; Accepted 2 April 2015

ABSTRAK

Metil ester berhasil diproduksi dengan transesterifikasi minyak nyamplung menggunakan katalisator kalsium oksida. Proses transesterifikasi dilakukan dalam suatu reaktor batch yang dilengkapi dengan pemanas, termokopel, pengaduk, termostat, dan pengambil sampel. Reaksi selanjutnya dilakukan selama 120 menit dan sampel diambil setiap 10 menit. Pengaruh parameter operasi yang berbeda seperti rasio molar metanol minyak, pemuatan katalis, suhu reaksi, dan waktu reaksi dievaluasi. Sebesar 82,53% konversi diperoleh pada kondisi optimum 12: 1 rasio molar metanol minyak, 60˚C suhu reaksi, 5% berat katalis, dan 2 jam waktu reaksi. Model optimasi: $Y = 82{,}26 + 0{,}77A + 0{,}16\ B + 2{,}05C + 1{,}66\mathrm{D} - 3{,}34\mathrm{A}^2 - 2{,}34\mathrm{B}^2 - 2{,}40\mathrm{C}^2 - 4{,}07\mathrm{D}^2 - 0{,}95\mathrm{AB} - 0{,}47\mathrm{AC} - 1{,}25\mathrm{AD} - 5{,}41\mathrm{BC} + 3{,}64\mathrm{BD} - 0{,}94\mathrm{CD}$. *Model kinetika reaksi kimia disusun dan diselesaikan dengan MATLAB. Nilai faktor frekuensi tumbukan adalah 0,0974 dan 0,0003 (dm^3/gmol.min). Sementara itu, nilai energi aktivasi reaksi berturut-turut adalah 23,34 dan 10,63 KJ/mol.*

Kata kunci: katalis padat, minyak nyamplung, model kinetika, transesterifikasi

ABSTRACT

Calophyllum oil is a very potential source of methyl ester that can be processed through transesterification. This work was a study transesterification of calophyllum oil with the use of solid acid catalyst was conducted in a batch reactor. The reaction was carried out for 120 minutes; meanwhile samples were taken from the reactor every 10 minutes for free fatty acid analysis. The 82.53% conversion was obtained at the optimum condition of 12:1 methanol to oil molar ratio, 60˚C reaction temperature, 5 wt% catalyst, and 2 h duration time. The method resulted in a model : $Y = 82{,}26 + 0{,}77A + 0{,}16\ B + 2{,}05C + 1{,}66\mathrm{D} - 3{,}34\mathrm{A}^2 - 2{,}34\mathrm{B}^2 - 2{,}40\mathrm{C}^2 - 4{,}07\mathrm{D}^2 - 0{,}95\mathrm{AB} - 0{,}47\mathrm{AC} - 1{,}25\mathrm{AD} - 5{,}41\mathrm{BC} + 3{,}64\mathrm{BD} - 0{,}94\mathrm{CD}$. In order to predict kinetics parameter of the transesterification reaction, a mathematical model of consecutive reactions was developed. The Matlab software was used to solve the simultaneous differential equations. Over the range of variables used in the experiment, the mathematical model was able to fit the experimental data quite well. The calculation results showed that the values of collision frequency factor for the reversible reactions were 0.0974 and 0.0003 (dm^3/gmol.min). Meanwhile, the activation energies for the reversible reaction were 23.34 and 10.63 KJ/mol.

Keywords: solid catalyst, calophyllum oil, kinetics modeling, transesterfication

INTRODUCTION

Utilization of edible oils has given rise to certain concerns as some of them are important food chain materials. In other words, the production of methyl ester of human nutrition sources can cause a food crisis (Srinivasan, 2009). Thus, majority of researchers have used non-edible oils as feed stock. The main obstacle in methyl ester production is the high cost of production but this problem can be solved with the utilization of calophyllum oil as raw material.

Vegetable oils require some modification before used in diesel engines. While dilution, thermal cracking (pyrolysis), and micro-emulsification are various methods used to modify vegetable oil, transesterification is the most common conversion process. Vegetable oils price are more expensive than non edible oils. Therefore, researchers have focused on non edible or waste cooking oils as feed stocks to methyl ester production costs by 60–90% (Zhang *et al.*, 2010; Shivakumar *et al.*, 2011).

The utilization of different types of catalyst improves the reaction rate and final yield. There are various types of transesterification reactions such as homogeneous, heterogeneous, and non-catalyst reaction. But, each of them has their own advantages or disadvantages. Previous studies reported the effects of various variables on conversion of methyl

*Penulis untuk korespondensi

ester from low quality waste cooking oil and high free fatty acid with 12-tungstophosphoric acid (TPA) as catalyst. The Studies indicated that this kinds of catalyst is nontoxic, recyclable, inexpensive, user environmentally friendly (Kulkarni *et al.,* 2006). Another study work reported investigated methyl ester production from jatropha curcas oil in the calcium oxide catalyst. The reactions were carried out at transesterification conditions: catalyst amount 4 wt%, methanol/oil ratio 15:1, reaction temperature, 338 K and reaction time, 6 h. Among the catalysts, CaO showed the highest catalytic activity with 85% JCO conversion (Taufiq-Yap *et al.,* 2011).

Kinetic data are vital for process assessment and development. Kinetic models are essential in design of chemical reactors, in the study of chemical reactions and develop at catalyst. Many information exists on the transesterification kinetics of vegetable oils to methyl esters, including soybean, rapeseed, canola and palm oils (Wenzel *et al*., 2006; Singh and Fernando, 2007; Stamenkovic *et al*., 2008; Cao *et al*., 2009). In this work, nonlinear regression was used to predict constants rate for both forward and reverse reactions using Matlab2014a, based on a modified model from the literature (Issariyakul, 2006). Nonlinear regression is a form of regression analysis in which observational data are modeled by function which is nonlinear combination of the model parameters and depends on one or more independent variables. A computer-based method of simultaneous, nonlinear regression of a differential equation model to experimental time series presented an efficient and powerful way to determine rate constants, greatly minimizing the amount of experimental data required to parameterize kinetic models (McNevin *et al.,* 2006). The objective of this work was to develop an alternative approach to predict the rate constants of transesterification process using nonlinear regression, determined with Matlab2014a, which includes both forward and reverse reaction.

MATERIALS AND METHODS

Materials

Calophyllum oil was obtained from Kebumen region, Central Java with specification of free fatty acid 2.56% and water of content 0.201%. Methanol (purity >99.8% v/v) and calcium carbonate were obtained from Merck-Schuchardt (Indonesia).

Catalyst Preparation

Calcium oxide was obtained after calcination of pulverized calcium carbonate in a helium gas flow at 1273 K for 5 h, and then was employed for transesterification of calophyllum oil with methanol. Additionally, immersion of calcium oxide in methanol was carried out for the purpose of preparing the reference sample of calcium methoxide.

Characterization of Catalyst

The chemical composition of the collected catalyst was examined by means of X-ray diffraction (XRD), and IR spectroscopy. XRD was measured on a GBC EMMA using CuKα radiation, over a 2θ range from 20° to 70° with a step size of 0.02^o at a scanning speed of 2 min^{-1}. Measurement of IR spectrum was performed on JASCO FT/IR applying KBr pellet technique, with 4 cm^{-1} resolution over a scanning range of 400–4000 cm^{-1}. The morphologies of calcium oxide catalysts were observed by using a scanning electron microscope (SEM-EDS). The total surface area was calculated by the BET (Brunauer-Emmet-Teller) method using data on nitrogen adsorption at 77 K. Both the nitrogen adsorption and the calculation were carried out on *NOVA* 3200e *Gas Sorption Analyzer*.

Transesterification Reaction

The transesterification reaction was performed in a 500 mL three-neck flask. For each run, the methanol and catalyst mixture was preheated to the desired temperature. Next, calophyllum oil that was separately heated to a certain temperature was added to the mixture and stirred at 400 rpm mixing intensity. After the reaction was completed, the mixture was then heated to 90^oC for 3 h to allow for the evaporation of excess methanol. The reaction product was comprised of two layers; the upper layer was methyl ester while glycerin was in the lower layer. In addition, the catalyst was easily separated with a simple filtration process. The conversion of Calophyllum oil is calculated by the following equation :

$$\text{Conversion} = \frac{\text{FFA initial} - \text{FFA final}}{\text{FFA initial}} \text{ x } 100\% \cdots\cdots \quad (1)$$

where FFA initial and FFA final are the free fatty acid (FFA) values of feed and product, respectively.

Experimental Design

Investigating a five level four factor Central Composite Design (CCD) required 30 experiments in this study. The fractional factorial design included six center points, eight axial points, and 16 factorial points. The ranges and the design levels of each variable are given in Table 1. The performance of the process was evaluated by analyzing the transesterification reaction conversion as the response. The quadratic equation for optimization is given in the following equation:

$$Y = \beta o + \sum_{i=1}^{4} \beta i Xi + \sum_{i=1}^{4} \beta ii\, Xi^2 \sum_{i=1} \sum_{j=i+1}^{4} \beta ii Xi Xj + \varepsilon \ \ldots\ldots (2)$$

Where Y is the response, βo is constant coefficient, βi, βii, and βij are linear, quadratic and second order interaction coefficient, respectively. Xi and Xj are independent variables where ε is the error. The R-square and Adjust R-Square were determined by the following equations:

$$R^2 = 1 - \frac{SSresidual}{SSmodel + SSresidual} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

$$\text{R adj}^2 = 1 - \frac{\frac{\text{SSresidual}}{\text{DFresidual}}}{(\text{SSmodel+SS residual})/)\text{DFmodel+DFresidual})} \quad \ldots\ldots\ldots (4)$$

where SS and DF are the sum of square and degree of freedom, respectively. Minitab 16. was used for regression (ANOVA). R-Square is the most important factor in examining the variability of independent variables. Meanwhile, the F-test is for checking the statistical significance of the model (Montgomery, 2011). The number of experiments, experimental conditions and results are summarized in Table 1. An additional 16 runs which included (molar ratio of methanol to oil (6:1-18:1), catalyst amount (3-7 wt%), reaction temperature (40-80^{o}C), and duration time (60-180 min) were performed. A samples at different time intervals were collected to illustrate the effect of each variable on reaction conversion and to demonstrate the RSM modeling results.

Kinetic Modelling

The three-step and overall chemical reactions for methyl ester production are described in the following equations, respectively:

$$TG + CH_3OH \underset{k_4}{\overset{k_1}{\rightleftharpoons}} DG + R1COOCH_3 \quad \ldots\ldots\ldots (a)$$

$$DG + CH_3OH \underset{k_5}{\overset{k_2}{\rightleftharpoons}} MG + R2COOCH_3 \quad \ldots\ldots\ldots (b)$$

$$MG + CH_3OH \underset{k_6}{\overset{k_3}{\rightleftharpoons}} GL + R2COOCH_3 \quad \ldots\ldots\ldots (c)$$

Overall reaction :

$$TG + 3CH_3OH \underset{k_8}{\overset{k_7}{\rightleftharpoons}} GL + 3RCOOCH_3 \quad \ldots\ldots\ldots (d)$$

where TG, DG, MG, CH_3OH, GL, $RCOOCH_3$ are triglyceride, diglycerides, monoglycerides, methanol, glycerol, and fatty acid methyl ester (FAME), respectively.

Kinetic studies of calophyllum oil transesterification have been carried out at the optimum conditions of 12:1 molar ratio of methanol to oil, 60^{o}C reaction temperature, 5 wt% catalyst amount and 2 h reaction temperature. The reaction rate according to the following equation is:

$$\frac{dC_A}{dt} = -k_1.C_A.C_B + k_2.C_C.C_D \quad (5)$$

$$\frac{dC_B}{dt} = 3[-k_1.C_A.C_B + k_2.C_C.C_D] \quad (6)$$

$$\frac{dC_C}{dt} = k_1.C_A.C_B - k_2.C_C.C_D \quad (7)$$

$$\frac{dC_D}{dt} = 3[k_1.C_A.C_B - k_2.C_C.C_D] \quad (8)$$

The kinetics parameters for the proposed kinetic model were estimated using non linear regression by minimizing the standard errors between the experimental data and the kinetic model. The rate constant depends on activation energy, the dependency of the rate constant, k on temperature should fit the Arrhenius equation :

$$k = Ae^{-E/RT} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

$$\ln k = -\frac{Ea}{RT} + \ln A \quad \ldots\ldots\ldots\ldots\ldots\ldots (10)$$

The standard errors (SEE) or the root-mean-square of residuals for N data points are determined below :

$$SSE = \frac{1}{N}\sum_{j=1}^{N}(C\,\text{exp}\,riment_{j,i} - Ccalculate_{j,i})^2 \quad (11)$$

RESULTS AND DISCUSSION

Analysis of Calcium Oxide Catalyst

Measurement of XRD patterns provided significant data on the change of calcium oxide under the reacting condition for the transesterification of calophyllum oil. Therefore, characterization of the catalyst collected after the reaction is essential for discussion to identify the catalytically active phase. Figure 1 shows XRD pattern of the catalyst collected after the calophyllum oil was completely transesterified. Obvious peaks appeared with 5 h values of 32.24°, 37.38°, 53.9°, 64.12°, and 67.36°. Since the molar ratio of methanol-calophyllum oil in the present experiment was four times larger in comparison to the stoichiometric ratio, it was small wonder that a portion of calcium oxide was combined with methanol under the reacting condition calcium oxide catalyst.

IR spectra analysis was conducted to determine the functional groups of calcium oxide catalyst. The results of IR spectra analysis of calcium oxide catalysts calcined temperature of 1000^{o}C for 5 hours can be seen in Figure 2.

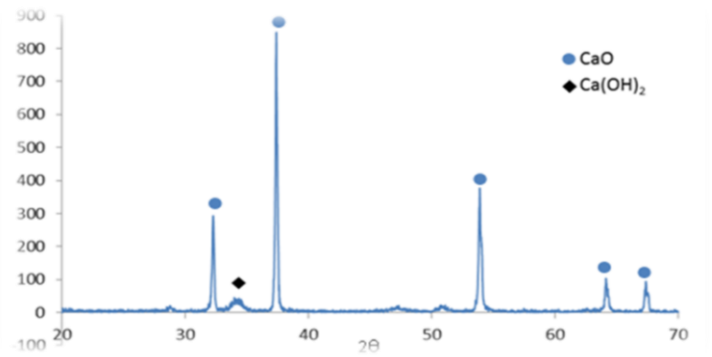

Figure 1. X-ray diffraction pattern of calcium oxide catalyst

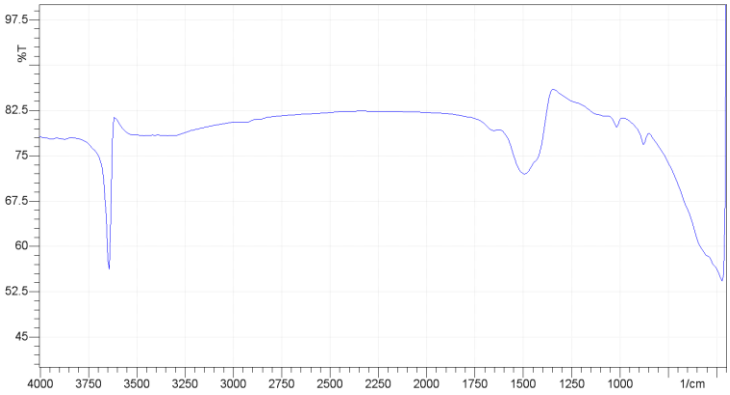

Figure 2. X-ray diffraction pattern of calcium oxide catalyst

Figure 2 show their IR spectra for calcium oxide indicate the presence of OH groups and CO_3^{2-} complex. CaO still has of OH complex group was a wave number of 3641. While the complex group CO_3^{2-} at wave number 1497 indicates that the catalyst calcium oxide (CaO) still contained carbonate content. While the complex group CO_3^{2-} at wave number 1497 indicates that the catalyst calcium oxide (CaO) still contained carbonate content.

Figure 3 shows the SEM-EDS images of CaO catalyst. The SEM images of CaO catalyst show aggregates of flat particles with size 10.2 µ, the morphologies of CaO catalysts can be considered of cubic crystalline phases. Particle shape does not give an indication of the chemical composition of the catalysts for the constituents. Results Disversive Energy Spectroscopy (EDS) showed that the catalyst component of calcium oxide (CaO) is composed of 32.5% Ca and 67.5% O_2

Surface area was calculated by the BET method using data on nitrogen adsorption at 77.35 K. Both the nitrogen adsorption and the calculation was carried out on Shimazu Tri-star 3000. The surface area of CaO catalyst was shown in Table 2. Surface area of CaO was 12.44 m^2 g^{-1}, total pore volume by 2,588e-01 cc/g and a pore size of catalyst 2018,5Å respectively. It was found that the catalysts with surface area were arranged in the sequence of MgO > CaMgO > CaZnO > CaO > Zn. The surface area of the catalyst determines the performance of the catalyst in the reaction of methyl ester formation.

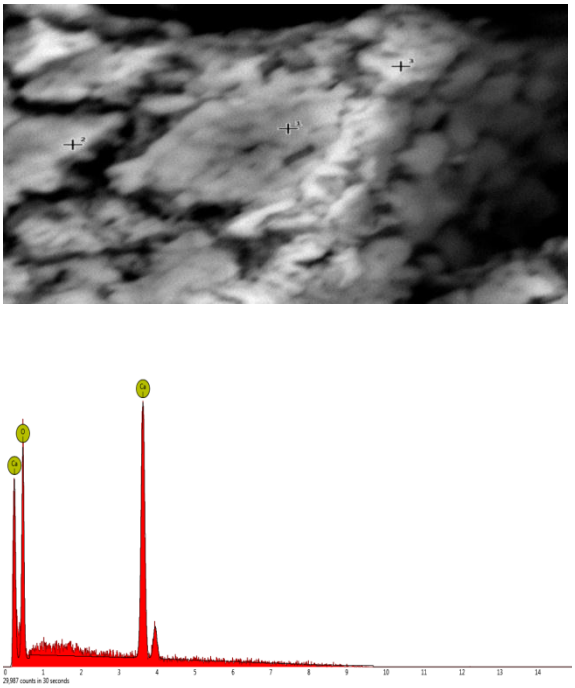

Figure 3. SEM-EDS image of calcium oxide catalyst calcined at 1000°C.

Table 2. BET Surface area of calcium oxide catalyst

BET Surface area of (CaO) (m^2 g^{-1})	Reference
0.56	West (1984)
6	Zhu (2006)
13	Kouzu (2008)
7.7	Fanny (2012)
12.44	in our work (2014)

Response Surface Methodology (RSM)

Fitting the data using different types of models such as linear, two factorial, quadratic, and cubic revealed that the transesterification of calophyllum oil and methanol in the presence of calcium oxide catalyst has been properly explained by the quadratic polynomial model. The best predicted FFA conversion models based on coded factors are shown in the following equation:

$$Y = 82.26 + 0.77A + 0.16\,B + 2.05C + 1.66\mathrm{D} - 3.34\mathrm{A}^2 - 2.34\mathrm{B}^2 - 2.40\mathrm{C}^2 - 4.07\mathrm{D}^2 - 0.95\mathrm{AB} - 0.47\mathrm{AC} - 1.25\mathrm{AD} - 5.41\mathrm{BC} + 3.64\mathrm{BD} - 0.94\mathrm{CD}$$

where the reaction temperature (A), duration time (B), methanol to oil molar ratio (C), and catalyst amount (D). The model F-value of 147,.36 implies that it is significant. There is only a 0.01% chance that a ‘‘Model F-Value’’ this large can occur due to noise. The value of ‘‘Prob > F’’ less than 0.05 indicates the model terms are significant. In this study A, B, C, D, A^2, B^2, C^2, D^2, AB, AC, AD, BC, CD are significant model terms. The ‘‘lack of fit F-value’’ of 3.79 implies the lack of fit is significant relative to pure error. The ‘‘predicted_R^2’’ of 0.9621. is in reasonable agreement with the ‘‘Adjusted R^2’’ of 0.9860. The suitable coefficient of determination (R^2 = 0.9621) infers that the quadratic model is highly significant and sufficient to represent the actual relationship between the variables and responses (Table 3).

Table 3. Central composite design of four independent parameters with experimental, RSM response values

Run	Temperature (^{0}C)	Time (min)	Molar Ratio (mole/mole)	Catalyst amount (%w/w)	FFA (%)	Conversion (%)
1	50	90	9	4	0.6276	75.5797
2	70	90	9	4	0.5758	77.5953
3	50	150	9	4	0.5823	77.3424
4	70	150	9	4	0.5656	77.9922
5	50	90	15	4	0.4976	80.6381
6	70	90	15	4	0.4432	82.7548
7	50	150	15	4	0.5881	77.1167
8	70	150	15	4	0.5673	77.9260
9	50	90	9	6	0.6121	76.1828
10	70	90	9	6	0.5799	77.4357
11	50	180	9	6	0.4721	81.6303
12	70	180	9	6	0.4692	81.7431
13	50	40	15	6	0.4797	81.3346
14	70	40	15	6	0.4896	80.9494
15	50	150	15	6	0.4978	80.6303
16	70	150	15	6	0.5073	80.2607
17	40	120	12	5	0.5598	78.2178
18	80	120	12	5	0.5215	79.7081
19	60	60	12	5	0.5132	80.0311
20	60	180	12	5	0.5165	79.9027
21	60	120	6	5	0.5713	77.7704
22	60	120	18	5	0.4615	82.0428
23	60	120	12	3	0.6019	76.5797
24	60	120	12	7	0.5165	79.9027
25	60	120	12	5	0.4489	82.5330
26	60	120	12	5	0.459	82.1400
27	60	120	12	5	0.4578	82.1867
28	60	120	12	5	0.4550	82.2957
29	60	120	12	5	0.4598	82.1089
30	60	120	12	5	0.4555	82.2762

Table 4. The results for ANOVA test

Source	DF	Seq SS	Adj MS	F-value	Prob>F
Regression	14	139.901	9.9930	147.36	0.000
Linear	4	45.438	11.3596	167.52	0.000
A	1	3.514	3.5136	51.81	0.000
B	1	0.153	0.1527	2.25	0.000
C	1	25.325	25.3252	373.46	0.000
D	1	16.447	16.4469	242.54	0.000
Square	4	48.368	12.0919	178.32	0.000
A*A	1	10.071	19.1664	282.64	0.000
B*B	1	4.170	9.3853	138.40	0.000
C*C	1	5.793	9.8754	145.63	0.000
D*D	1	28.334	28.3342	417.84	0.000
Interaction	6	46.095	7.6826	113.29	0.000
A*B	1	0.901	0.9014	13.29	0.002
A*C	1	0.216	0.2162	3.19	0.094
A*D	1	1.550	1.5504	22.86	0.000
B*C	1	29.316	29.3157	432.31	0.000
B*D	1	13.236	13.2360	195.19	0.000
C*D	1	0.876	0.8757		0.003
Residual Error	15	1.017	0.0678	12.91	0.077
Lack-of-Fit	10	0.899	0.0899	3.79	
Pure Error	5	0.119	0.0237		
Total	29	140.919			

Effect of Catalyst Loading on Transesterification Reaction

The effect of catalyst concentration on transesterification was investigated by varying the catalyst loading from 2 to 6 wt% based on the weight of calophyllum oil (Figure 4a). The reaction conversion increased as the catalyst amount was increased up to 5 wt%. Figure 1a illustrates that reaction conversion increased from 3.27% to 62.84% for 2 wt% catalyst and also it increased from 21.44% to 84.79% for 5 wt% at 2 h reaction time. However, the conversion decreased with excess loading due to increased viscosity of the reaction mixture. Zhang *et al.* (2010) reported similar effect on conversion. Meanwhile, Taufiq-Yap *et al.* (2011) reported that when the catalyst dosage was too much, more biodiesel products were absorbed by catalysts, and as a result, final conversion decreased. A contour plot (Figure 4b) represents the conversion as a function of catalyst loading and molar ratio at 2 h and 60^{o}C. Higher molar ratio deactivated the catalyst and reversed the reaction to the reactant side. Mass transfer effect of solid catalyst could also be a factor in the decreasing conversion Taufiq-Yap *et al.* (2011). Srilatha *et al.* (2009) reported a similar trend for the effect of molar ratio and catalyst on reaction conversion.

Effect of Methanol to Oil Molar Ratio on Transesterification Reaction

Theoretically the transesterification reaction needs only three moles methanol and one mole oil at the presence of catalyst for completion. However, the transesterification is reversible and higher amounts of methanol to oil molar ratio can shift the equilibrium to the product side and increase the conversion. The researcher attempt to evaluate the wide range of methanol to oil molar ratio in this study which includes (6:1, 9:1, 12:1, 15:1, 18:1). Figure 5 illustrates the methyl ester conversion increased as the methanol to oil molar ratio increases and reaches 84.79% at 12:1 molar ratio. The conversion did not vary appreciably above this molar ratio. Methyl ester production from high free fatty acid calophyllum oil by solid calcium oxide catalyst.

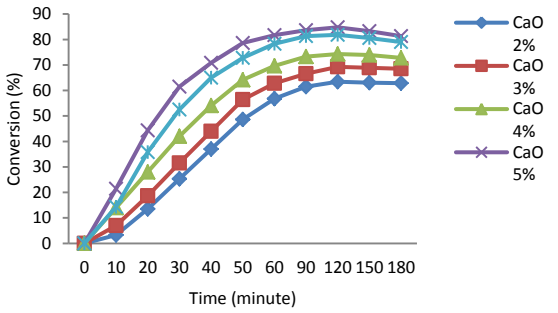

Figure 4a. Effect of catalyst amount on conversion of metil ester (molar ratio of methanol to oil = 12:1, reaction temperature = 60^{o}C).

Effect of Reaction Temperature on Transesterification Reaction

The reaction was carried out at five different temperatures ranging from 40^{o}C to 80^{o}C in order to find the influence of temperature on reaction conversion (Figure 6). The conversion increased dramatically as the temperature increased between 40^{o}C and 60^{o}C. In fact, the conversion ramped from 8.95% to 64.20% at 40^{o}C and from 26.85% to 84.83% at 60^{o}C. The results are in good agreement with other studies such as Wei *et al.* (2009) who obtained the high yield (>95%) at the optimum temperature of 60^{o}C.

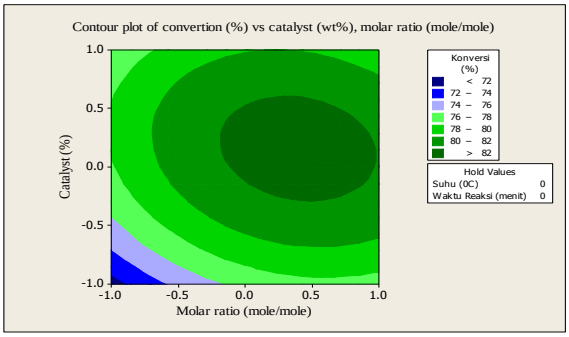

Figure 4b. Interaction of methanol-oil ratio versus catalyst loading (reaction time = 2 h, reaction temperature = 60°C).

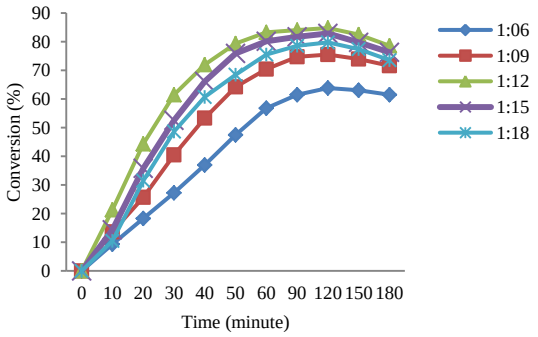

Figure 5. Effect of molar ratio amount on conversion of methyl ester (catalyst consentration 5 wt%, reaction temperature = 60°C).

However, the conversion decreased for temperatures beyond 60°C which can be attributed to chemical reactions. During the frying process, three types of chemical reactions, hydrolytic, oxidative, and thermolytic, occurred. These reactions created some undesirable components such as some polymerized triglycerides and FFA that led to a negative effect on transesterification conversion (Cao, 2008). Meanwhile, Birla *et al.* (2011) reported that for temperatures higher than the methanol boiling point of 65°C, the solvent vaporized, thus, methanol remained in the vapor phase in the reactor and was less available in reaction environment.

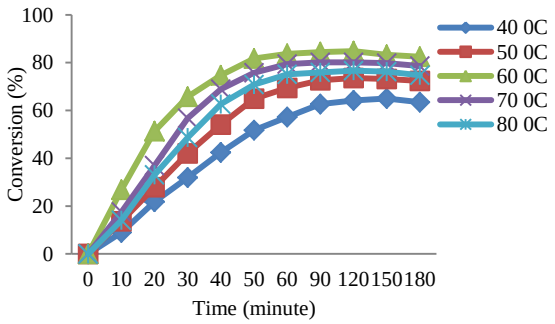

Figure 6. Effect of temperatur amount on conversion of methyl ester (catalyst consentration 5 wt%, malor ratio 12:1)

Kinetic Study: Transesterification Calophyllum Oil and Methanol

In this study, the kinetics calculations performed on the basis of the transesterification reaction stoichiometry. From the data conversion (XA) and measurement of fatty acids free residual (CA) obtained CB, CC, and CD as shown in Figure 7.

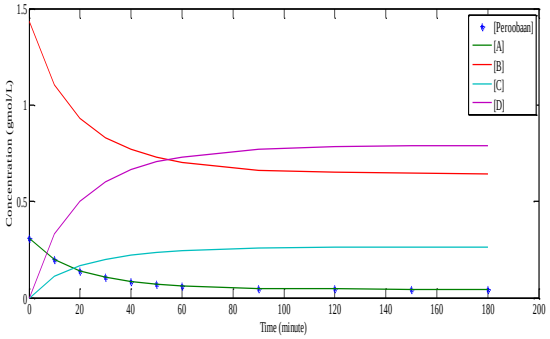

Figure 7. Concentration (gmol/L) and time (minute) at 60°C ([A] = calophyllum oil nyamplung, [B] = methanol, [C] = glycerol, dan [D] = methyl ester (FAME)

Figure 8 show the concentration dynamic changes of calophyllum oil, methanol, glycerol and methyl ester vs. time. The points represent experimental data and the solid curves represent the calculated results utilizing the kinetic model consisting of two reactions which includes forward and reverse reversible reactions. Analysis of the figures show that calophyllum oil continuously decreases and at methyl esters concentration increased rapidly during the first 20 min reaching a maximum and after that slowly constans. It is seen that the rate of reactant concentrations increased progressively down and products. Value of the reaction rate constant (k1) at 40, 50, 60, 70 and 80°C of 0.0120, 0.0174, 0.0357, 0.0250, and 0.0212 dm^3/gmol.min, respectively, greater compared to the value of the reaction rate constant (k2) 0.0074, 0.0055, 0.0047, 0.0044, and 0.0053 dm^3/ gmol.min, respectively, it shows the change in the concentration of the reactants towards the formation of the product.

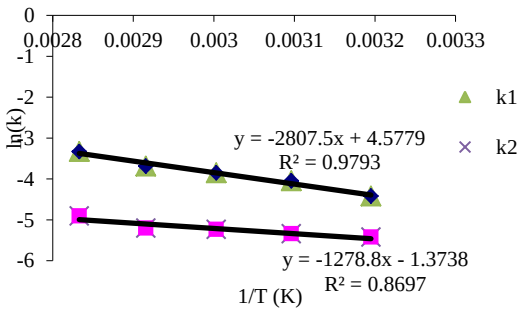

Figure 8. The linear relationship between ln k versus time according to Arrhenius equation

Activation energy calophyllum oil transesterification process and methanol using a linear graph the relationship between ln k with 1/T, based on the equation ln k = ln A - Ea / RT, can be seen in Figure 7. The value of the activation energy (Ea1) = 23.34 KJ / mol and the pre-exponential factor (A1) = 0.0973 m^3 / gmol.menit on k1 greater than the activation energy (Ea2) = 15.14 KJ/mol and pre-exponential factor (A2) = 2,531x10^{-4} m^3/gmol.min on k2. This shows that the transesterification reaction is reversible, the activation energy (Ea1) and collision factor (A1) required to produce the desired product is greater than the activation energy (Ea2) is required to change the product back to reactants. Evidence supporting the kinetic parameters of the current model is a statistical evaluation of the kinetic model as shown in Table 4. The model exhibits good statistical correlation with a sum of squares error (SSE) of 9.54x10^{-5}, RMSE of 1.91x10^{-2}, Chi-square (X^2) of 1.17x10^{-4} and R^2 0.9941.

CONCLUSIONS AND RECOMMENDATION

Conclusions

The highest experimental conversion of colophyllum oil to methyl ester was 82.53% at the optimum condition of 2 h reaction time, 12:1 molar ratio of methanol to oil, 60^{o}C reaction temperature, and 5 wt% catalyst loading, and RSM (R^2 = 0.9621). The ANOVA results revealed that the molar ratio of methanol to oil was the most important variable. A mathematical model describing chemical kinetics of transesterification of calophyllum oil with methanol has been developed. The model was developed by utilizing nonlinear regression method, which is an efficient and powerful way to determine rate constants for both forward and reverse reactions. A comparison with previous study which excludes the reverse reactions was made. The reaction rate constants were determined using MATLAB 2014a and the ratios of rate constants obtained were well in agreement with those reported in the literature. A good correlation between model simulations and experimental data was observed. It was proven that both methods were able to predict the rate constants with plausible accuracy.

Recommendation

One of the most important features for a catalyst to be industrially useful is its stability and reusability. For practical use of the solid base catalyst, we will go on investigating the reusability catalysis of calcium oxide in our future work.

Table 4. Statistical analysis for kinetic models

	Temperature (^{o}C)				
	40	**50**	**60**	**70**	**80**
SSE	1.18x10^{-4}	1.94x10^{-4}	9.54x10^{-5}	3.46x10^{-4}	2.66x10^{-4}
RMSE	3.86x10^{-2}	3.64x10^{-2}	1.91x10^{-2}	3.73x10^{-2}	3.74x10^{-2}
X^2	1.44x10^{-4}	2.37x10^{-4}	1.17x10^{-4}	4.23x10^{-4}	3.25x10^{-4}
R^2	0.9963	0.9925	0.9941	0.9834	0.9885

REFERENCE

Birla A, Singh B, Upadhyay SN, Sharma YC. 2011. Kinetics studies of synthesis of biodiesel from waste frying oil using a heterogeneous catalyst derived from snail shell. *Biores Technol:* 106: 95-100.

Cao F, Chen Y, Zhai F, Li J, Wang J, Wang X. 2008. Biodiesel production from high acid value waste frying oil catalyzed by superacid heteropolyacid. *Biotech Bioeng*. 101:93–100.

Cao P, Tremblay AY, and Dube MA. 2009. Kinetics of canola oil transesterification in a membrane reactor. *Indust Eng Res.* 48: 2533–2541.

Fanny WA, Subagjo, dan Prakoso T. 2012. Pengembangan Katalis Kalsium Oksida untuk Sintesis Biodiesel. *J Tek Kim Indo.* 11 (2): 66-73.

Issariyakul T. 2006. Biodiesel Production from Fryer Grease. MSc diss. Department of Chemical Engineering, University of Saskatchewan.

Jain S, Sharma MP, and Rajvanshi S. 2011. Acid base catalyzed transesterification kinetics of waste cooking oil. *Fuel Process Technol*. 92:32–38.

Kiakalaieh AT, Amin NAS, Zarei A, Iman Noshadi I. 2013. Transesterification of waste cooking oil by heteropoly acid (HPA) catalyst: Optimization and kinetic model. *Appl Energy*. 102: 283–292.

Kouzu M, Kasuno T, Tajika M, Sugimoto Y, Yamanaka S, Hidaka J. 2008. Calcium oxide as a solid base catalyst for transesterification of soybean oil and its application to biodiesel production. *Fuel*. 87(12): 2798 – 2806.

McNevin D, Caemmerer S, and Farquhar G. 2006. Determining RuBisCO activation kinetics and other rate and equilibrium constants by simultaneous multiple nonlinear regression of a kinetic model. *J Experimen Bot.* 57 (14): 3883–3900.

Montgomery DC. 2011. *Design and Analysis of Experiments, Student Solutions Manual*. 5th ed. New York: John Wiley & Sons, Ltd.

Srinivasan S. 2009. The food v fuel debate: a nuanced view of incentive structures. *Renew Energy*. 34(4):950–954.

Shivakumar, Pai PS, and Shrinivasa BR. 2011. Artificial neural network based prediction of performance and emission characteristics of a variable compression ratio CI engine using WCO as a biodiesel at different injection timings. *Appl Energy*. 88:2344–2354.

Srilatha K, Lingaiah N, Devi BLAP, Prasad RBN, Venkateswar S, Prasad PSS. 2009. Esterification of free fatty acids for biodiesel production over heteropoly tungstate supported on niobia catalyst. *Appl Catal A: Gen.*365: 28e33.

Singh AK and Fernando SD. 2007. Reaction kinetics of soybean oil transesterification using heterogeneous metal oxide catalysts. *Chem Eng.* 30 (12): 1716–1720.

Stamenkovic OS, Todorovic ZB, Lazic ML, Veljkovic VB, Skala DU. 2008. Kinetics of sunflower oil methanolysis at low temperatures. *Biores Technol.* 99:1131–1140.

Taufiq-Yap YH, Lee HV, Hussein MZ, Yunus R. 2011. Calcium-based mixed oxide catalysts for methanolysis of Jatrophacurcas oil to biodiesel. *Biomass Bioenergy*. 35:827–834.

Tan KT, Gui MM, Lee KT, Mohamed AR. 2010. An optimized study of methanol and ethanol in supercritical alcohol technology for biodiesel production. *J Supercrit Fluids.*53:82–87.

Tesser R, Di Serio M, Guida M, Nastasi M, Santacesaria E. 2005. Kinetics of oleic acid esterification with methanol in the presence of triglycerides. *Ind Eng Chem Res*. 44:7978–7982.

Wei Z, Xu C, and Li B. 2009. Application of waste eggshell as low-cost solid catalyst for biodiesel production. *Biores Technol*. 100:2883–2885.

Wenzel B, Tait M, Modenes A, Kroumov A. 2006. Modelling chemical kinetics of soybean oil transesterification process for biodiesel production: an analysis of molar ratio between alcohol and soybean oil temperature changes on the process conversion. *Bioautomation* 5:13–22.

Yan S, Kim M, Mohan S, and Salley SO. 2009. Oil transesterification over calcium oxides modified with lanthanum. *Appl Catalysis A: General*. 360: 163–170.

Zhu H, Wu Z, Chen Y, Zhang P, Duan S, Liu X, Mao Z. 2006. Preparation of biodiesel catalyzed by solid super base of calcium oxide and its refining process, *Chinese J Catalysis*. 27(5): 391 – 396.

Zhang L, Sheng B, Xin Z, Liu Q, Sun S. 2010. Kinetics of transesterification of palm oil and dimethyl carbonate for biodiesel production at the catalysis of heterogeneous base catalyst. *Biores Technol*. 101:8144–8150.